Preface

Graphene sheets, one atom thick, two dimensional layers of carbon atoms, have gained enormous importance over the past few years due to their unique attributes - high electronic, thermal conductivities and exceptional mechanical strength. Chemical reduction of graphene oxide (GO) has been considered as a viable route for large scale production of graphene sheets. The reduced graphene oxide (r-GO) sheets although their conductivities are comparatively lower than that of graphene are nevertheless versatile material for applications in thin films and composites. An important consideration in the design of solution processing techniques for the preparation of processable graphene sheets is the dispersibility of GO and r-GO in different solvents, especially aqueous dispersibility. While GO is dispersible in water over a wide range of pH values, r-GO shows poor dispersibility and over a limited range of pH values.

Graphene oxide, the oxidized form of graphene, are single atomic layers with lateral dimension that can extend to hundreds of nanometers. The sheets contain a sizable fraction of carbons that are sp^3 hybridized and covalently bonded to oxygen in the form of epoxy, carbonyls as well as ionizable hydroxyl and carboxylic functional groups located on the rim of the sheets. The remaining carbons form isolated sp^2 graphene like networks. On reduction the oxygen functionalities are removed and the sp^2 network partially restored. This thesis focuses on the aqueous dispersibility of GO and r-GO, and describes a strategy to enhance the dispersibility of r-GO by cyclodextrin functionalization. **Chapter 1** of the thesis provides a brief review of the synthetic procedures and structure of GO and r-GO while **Chapter 2** describes the experimental methods and characterization techniques used in the thesis.

The chemistry underlying the aqueous dispersibility of GO and r-GO at different values of pH have been investigated by zeta potential measurements, pH titrations and infrared spectroscopy (**Chapter 3**). These measurements show that r-GO sheets have

ionizable groups with a single pKa value (8.0) while GO sheets have groups that are more acidic (pKa = 4.3), in addition to groups with pKa values of 6.6 and 9.0. Infrared spectroscopy has been used to follow the sequence of ionization events. In both GO and r-GO sheets, it is ionization of the carboxylic groups that is primarily responsible for the build up of charge, but on GO sheets, the presence of phenolic and hydroxyl groups in close proximity to the carboxylic groups lowers the pKa value by stabilizing the carboxylate anion, resulting in superior water dispersibility.

Till recently GO was primarily considered only as an easily available precursor for chemical routes to r-GO but it has now been recognized as an interesting material in its own right. Two such attributes that have attracted wide spread attention are the intrinsic and tunable fluorescence of GO as well as formation of liquid crystalline phases. Aqueous dispersions of GO exhibit strong pH dependent fluorescence in the visible region that originates, in part, from the oxygenated functionalities present. In **Chapter 4**, the spectral migration on nanosecond timescales of the pH dependent features in the fluorescence spectra of GO is described. The changes in the steady state fluorescence spectra with pH have been correlated with the sequence of dissociation events that occur in GO dispersions at different values of pH described in **Chapter 3**, from time resolved emission spectra (TRES) constructed from the wavelength dependent fluorescence decay curves, it is shown that the migration is associated with excited state proton transfer. Both 'intramolecular' and 'intermolecular' transfers involving the quasimolecular oxygenated aromatic fragments are observed.

Aqueous dispersions of GO constitute a distinctive class of 2D-anisotropic colloids with competing interactions - long range electrostatic repulsion, originating from ionized carboxylic groups located on the rim of the sheets and weak dispersive attractive interactions originating from the un-oxidized sp^2 graphitic domains. In **Chapter 5**, it is shown that, colloidal dispersions of GO are intrinsically frustrated, exhibiting a range of arrested or metastable states, encompassing fluid, glass and gels that coexist with liquid crystalline order. These states can be accessed by varying the relative magnitudes of the repulsive and attractive forces by changing the ionic strength of the medium, by addition of salt and/or the concentration of the dispersion. At low salt concentrations, where long range electrostatic repulsions dominates, the formation of a repulsive Wigner glass is observed while at high salt concentrations, when attractive forces dominate, the formation of gels that

exhibits a nematic to columnar liquid crystalline transition. These studies highlights how the chemical structure of GO - hydrophilic ionizable groups and hydrophobic graphitic domains coexisting on a single sheet - gives rise to a rich and complex phase diagram.

The poor dispersibility of *r*-GO in aqueous media limits its use in practical applications. To enhance the dispersibility, *r*-GO sheets have been functionalized by covalently linking β-cyclodextrin (β-CD) cavities to the sheets via an amide linkage (**Chapter 6**). The functionalized β-CD: *r*GO sheets, in contrast to *r*-GO, are dispersible over a wide range of pH values (2 - 13). Zeta potential measurements indicate that there is more than one factor responsible for the dispersibility. It is shown that planar aromatic molecules adsorbed on the *r*-GO sheet as well as nonplanar molecules included in the tethered β-CD cavities have their fluorescence effectively quenched by the β-CD: *r*GO sheets. The β-CD: *r*GO sheets combine the hydrophobicity associated with *r*-GO along with the hydrophobicity of the cyclodextrin cavities in a single water dispersible material.

Resonance Raman spectroscopy is a powerful analytical tool for detecting and identifying analytes, but the associated strong fluorescence background severely limits the use of the technique. In **Chapter 7**, it is shown that the cyclodextrin functionalized β-CD: *r*GO sheets, described in **Chapter 6**, provides a versatile platform for resonance Raman detection. Planar aromatic and dye molecules that adsorb on the *r*-GO graphitic domains and non-planar molecules included within the tethered β-CD cavities have their fluorescence effectively quenched. Using the water dispersible β-CD: *r*GO sheets, it is possible to record the resonance Raman spectra of adsorbed and included organic chromophores directly in aqueous media without having to extract or deposit on a substrate. The Raman signal intensities show a linear dependence with the concentration of analyte present in water. This is significant, as it allows for the identification and estimation of organic analytes present in water by resonance Raman spectroscopy.